

LIFETIMES OF ELECTRODES FOR AMTEC CELLS

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ABSTRACT

The lifetime of an AMTEC electrode depends on the rate of grain growth, which in turn depends on the surface self-diffusion coefficient of the electrode material under AMTEC operating conditions. Grain growth rates for molybdenum and platinum-tungsten alloy electrodes have been determined, and have been used to predict operating lifetimes of AMTEC electrodes. For lifetimes of 10 years or more, Mo may be used in AMTEC cells only at operating temperatures under 1100 K. Pt_2W electrodes may be used at much higher temperatures, up to 1300 K.

INTRODUCTION

AMTEC, the Alkali Metal Thermal to Electric Converter, is a direct energy conversion device capable of near-Carnot efficiencies. Single cells have performed at high power densities, with open circuit voltages up to 1.6 V and current densities up to 2.0 A/cm^2 [1-3]. Efficiencies as high as 13-15% have been reported [4]. The device is an alkali metal concentration cell which uses a γ -alumina solid electrolyte (BASE) tube as a separator between a high pressure region containing liquid metal (generally sodium) at 900 - 1300 K and a low pressure region containing a condenser at 400-700 K. BASE is an ionic conductor; alkali metal is oxidized at the liquid metal/BASE interface and alkali metal ions are transported to the low pressure side of the BASE. Electrons travel through an external load to recombine with transport ions at a porous film metal electrode ($0.7 - 1 \mu\text{m}$ thick) deposited on the outside wall of the BASE tube; alkali metal vapor leaves the electrode and is collected on a condenser at 400-700 K.

For an AMTEC device to be feasible for either space or terrestrial applications, it must have a minimum operating lifetime of 5-10 years. Tests done in AMTEC research have shown that, on the time scales studied (up to 8000 hours), the electrode is the component most likely to influence device

performance and limit operating lifetime. The ideal AMTEC electrode is one which has three primary characteristics: (1) it is thin enough to allow ready transport of sodium atoms from the electrode-electrolyte interface to the low pressure side of the electrode, for vaporization and transport to the condenser, (2) it is thick enough to offer good electrical conductivity for the electrons traveling from the external circuit to the interface where recombination of electrons and sodium ions takes place, and (3) it has a lifetime which will allow continuous operation for a minimum of five years, and preferably for ten or more years.

Electrodes used in AMTEC cells at JPL have included refractory metal and metal alloy electrodes, including molybdenum, tungsten, rhodium-tungsten and platinum-tungsten. Other researchers have studied titanium nitride, titanium carbide, niobium nitride and niobium carbide as electrode materials and found them to be promising as high power-density electrodes [5,6]. This paper considers the characteristics of molybdenum and of tungsten alloy electrodes, and predicts operating lifetimes of those materials as AMTEC electrodes based on data taken during several hundreds or thousands of hours of AMTEC operation.

ELECTRODE LIFETIME

Electrode lifetime is the period over which electrode performance is sufficient for high efficiency device operation; it is defined here as the time for electrode grains to grow to a diameter $\phi - 1 \mu\text{m}$. This value has been chosen because of the relationship between grain diameter and temperature independent exchange current in an operating AMTEC electrode [7].

A model of electrode lifetime based on metal grain growth rates has recently been developed at JPL [8]. This model presumes growth to proceed as the coalescence of spheres with conservation of volume and that the mechanism of grain growth is surface self diffusion alone. Electrode materials

have been chosen to have vapor pressures below 1×10^{-9} Pa at temperatures up to 1200 K, keeping evaporation and volume diffusion rates low. A magnetron sputtered metal or metal alloy film is initially columnar; however, evolution of columns to spheres proceeds at the same rate as sphere coalescence in the absence of evaporation and volume diffusion [9].

The operable lifetime of an electrode may be predicted using the Herring Law [9-11] to determine the grain growth rate, expressed as the time, t , for two spheres to coalesce. The time is related to the initial radius (R_i) of the spheres by the Herring law:

$$t = \frac{0.89 R_i^4}{D_s N_0 \gamma_0 \Omega^2 / kT} \quad (1)$$

where D_s is the surface self-diffusion coefficient of the electrode material (cm^2/s), N_0 is the atom density of electrode material on the surface of the electrolyte (atoms/cm^2), γ_0 is the surface energy of the material (J/cm^2), Ω is the atomic volume of the material (cm^3/atom), k is the Boltzmann constant and T is the temperature (K). D_s may be calculated for a material from measured grain growth over a measured time at a single temperature. N_0 is calculated from the atomic volume as $N_0 = \Omega^{-2/3}$ [9]. The other factors may be, or have been, measured directly.

Lifetime is related to grain growth rate through the temperature independent exchange current, B . The exchange current is the reversible oxidation-reduction reaction which takes place at the electrode-electrolyte interface, and is related to the contact made by electrode grains with the electrolyte. The electrode reaction, reduction of

sodium ions (Na^+), occurs at the interface, either under or at the perimeter of the grains. As grain size increases, total material volume is conserved and the number density of grains, and thus total contact between grain and electrolyte, decreases. A temperature independent exchange current, B has been defined as $B = j_0(T^{\alpha}/P)$ where j_0 is the exchange current determined from electrochemical measurements, T is the electrode temperature and P the alkali metal pressure.

Exchange current is proportional to grain size, either to contact perimeter ($2\pi R$) or to contact area (πR^2), and thus will decline as the total number of grains declines. As radius increases according to Equation (1), the total contact will decrease and B will decline as either $t^{1/4}$ or $t^{1/2}$.

Typical sputter deposited electrodes have a starting grain diameter of $0.1 \mu\text{m}$, an initial grain volume of V_i . The surface coverage is ~80%. After 10 rounds of coalescence, the volume of an individual grain has increased to $\sim 1000V_i$, grain diameter has increased to $\sim 1 \mu\text{m}$, and surface coverage has fallen to $\sim 8\%$ (voids account for $\sim 92\%$ of the projected electrode surface area.)

Figure 1 shows a sketch of voids opening in an electrode as grains coalesce. From a surface coverage of 52% in (a) (voids account for 48% of the projected area), two rounds of coalescence result in a decrease to 33% surface coverage in (c).

As grain size increases, the total number of grains decreases and thus total contact area between grains and electrolyte decreases. When grains reach a diameter of $1 \mu\text{m}$, the total contact area has decreased by a factor of 10.

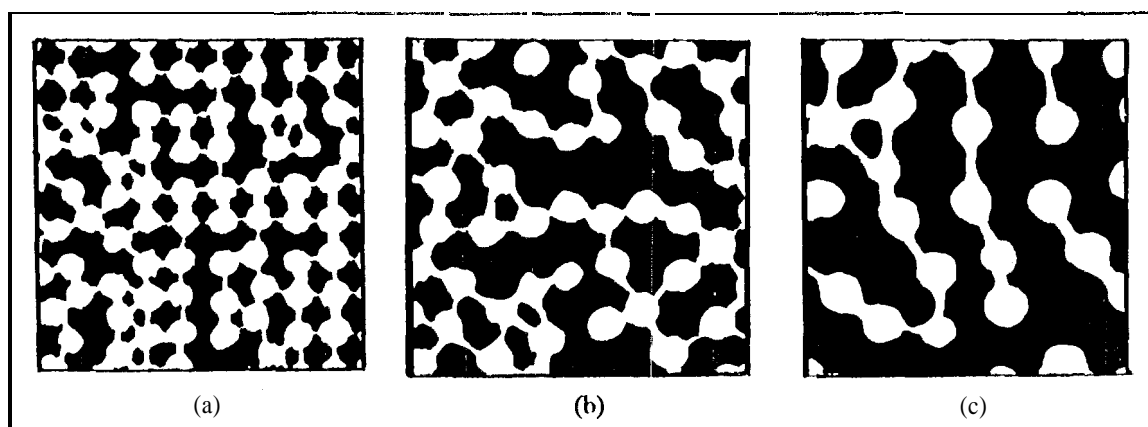


Figure 1: As grains grow by coalescence, voids open in the electrode surface. In (a), grain radius $R = R_i$, grain volume $V = V_i$; (b) $R = 1.26R_i$ and $V = 2V_i$; (c) $R = 1.59R_i$ and $V = 4V_i$.

Both the total contact area and the surface coverage influence the performance of the electrode. As voids open, electrical conductivity within the electrode decreases, until finally, grains are not connected and there can be no conduction from grain to grain. In addition, the magnitude of the exchange current depends on the area available for the reaction to take place, the contact area.

Figure 2 shows a semi-empirical plot of electrode power vs. exchange current. B has been shown to be ~ 120 for several electrode materials and compositions [12]; a decrease in B to ~ 25 will result in a decrease in power to $\sim 70\%$ of initial power. As can be seen in the plot, exchange current can fall significantly without serious effect on the electrode output power. If lifetime is defined as the time it takes for grains to grow to a diameter of $0.5 \mu\text{m}$, B will fall to $\sim .5B_i$ and power will fall to ~ 0.91 . If lifetime is defined as the time for grains to grow to a diameter of $1.0 \mu\text{m}$, B will fall to $\sim 0.2B_i$ and power will fall to $\sim 0.7P_i$.

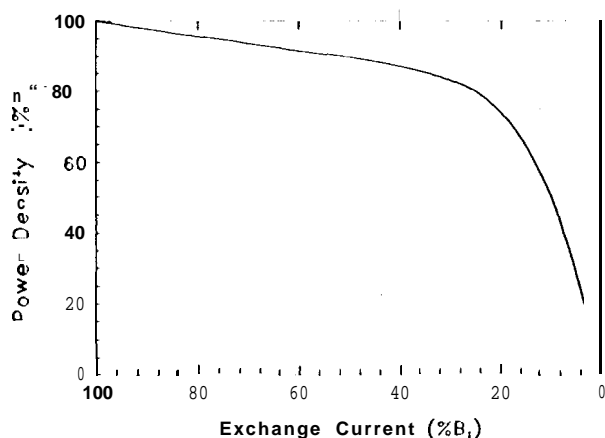


Figure 2: Electrode power vs. Exchange Current (B). Electrode power falls off slowly with exchange current until voids open in the electrode and B falls below 20% of B_i .

Prediction of electrode lifetime requires experimental determination of the rate of grain growth at various temperatures. These data may be used to calculate surface self-diffusion coefficients (D_s), which, when fitted to an Arrhenius plot allow the development of an equation to calculate D_s at any temperature covered by the plot. The calculated surface self-diffusion coefficient may then be used to determine the rate of grain growth and predict the time for grains to grow to a diameter of $1 \mu\text{m}$.

Several AMTEC experiments have been run using molybdenum as well as tungsten alloy electrodes (platinum-tungsten and rhodium-tungsten). Surface self-diffusion coefficients have been determined for Mo, Pt-W and Rh-W electrodes over a wide range of temperatures (1000-1200 K) using the Herring Sealing Law and measured grain size before and after operation of electrodes in AMTEC cells. The diffusion coefficient for Rh-W films has been determined for a single temperature within the operating range of an AMTEC device. Comparison of these diffusion coefficients determined in sodium vapor with coefficients determined in vacuum show an increase of approximately a factor of four in the surface self-diffusion coefficient as a result of exposure to sodium vapor atmosphere.

EXPERIMENT AND RESULTS

Electrodes were deposited on sodium β -alumina solid electrolyte (BASE) tubes (Ceramtec) by d.c. magnetron sputtering. The tubes were masked to define electrodes of a predetermined area. The prepared tubes were contacted with a current collection network and mounted in an AMTEC Electrode Test Cell (ETC), which has previously been described in detail [13-15]. The tube is heated by an internal resistance heater, which does not deliver heat uniformly over the entire length of the BASE tube.

Three molybdenum electrodes were run on the same Na-BASE tube in a liquid-fed AMTEC experiment for ~ 200 hours. The temperature of the three electrodes were 1135 K, 1190 K, and 1202 K. Initial grain size was $\phi \sim .2 \mu\text{m}$; grain diameters after operation were determined by Scanning Electron Microscopy. Surface self-diffusion coefficients (D_s) for Mo in sodium atmosphere were calculated from Equation 1, then plotted as $-\ln(D_s)$ versus $1/T$. The fitted line shows very good Arrhenius behavior with an activation energy $E_a = 8.44 \text{ eV}$ and a pre-exponential factor $A = 2.5 \times 10^{26}$. D_s for molybdenum has been verified in another experiment at 1200 K. Using the Herring Law, the time for grains to grow to a chosen diameter ϕ may be determined. Figure 3 shows a plot relating growth time to temperature. Plots for time for grains to grow to $\phi = 0.5 \mu\text{m}$ and to $\phi = 1.0 \mu\text{m}$ are included in Figure 3. Using these data, we can determine that at an operating temperature of 1125 K, a lifetime of ~ 6 years may be expected for a molybdenum electrode if the end of life is when grains reach $\phi = 1 \mu\text{m}$ and less than 1 year if end of life is when grain diameter reaches

0.5 μm .

Similarly, a $\text{Pt}_{2.5}\text{W}$ electrode was operated -2000 hours at constant temperature. The temperature varied across the sample, so it was possible to take electrode samples which had been operated at 1050, 1066, 1098, 1106, and 1114 K. These samples were analyzed as the molybdenum samples and a surface self-diffusion coefficient in sodium vapor determined. An Arrhenius plot of these data yields an activation energy $E_A = 2.97$ eV and a pre-exponential factor $A = 0.46$. Figure 4 relates time and temperature for $\text{Pt}_{2.5}\text{W}$. As may be seen from this plot, a lifetime $\gg 100$ years is predicted for $\text{Pt}_{2.5}\text{W}$ at 1125 K and a lifetime of 10 years for operation at 1300 K for grain diameters of 1 μm . For end-of-life grain diameters of 0.5 μm , the lifetime of $\text{Pt}_{2.5}\text{W}$ will be 60 years at 1125 K and 10 years at 1200 K.

Similar calculations have been made at a single temperature for Rh_2W electrodes. The surface self-diffusion coefficient for Rh_2W at 1125 K is $\sim 1 \times 10^{-12}$ cm^2/s , which may be used to predict a lifetime of 20 years for Rh_2W electrodes at that temperature.

CONCLUSION

Molybdenum is a well studied electrode, but grain growth is too rapid for device applications at temperatures above 1100 K. AMTEC devices which are designed for lower temperature operation may use molybdenum electrodes, although real time verification of the predicted lifetimes would be desirable. Platinum-tungsten alloy electrodes have much slower grain growth than molybdenum, and may be operated for long periods at temperatures approaching 1200 K. It has previously been determined that AMTEC electrode performance for platinum-tungsten alloy electrodes is highly dependent on the platinum-tungsten ratio [8], and it may be expected that the rate of grain growth will increase significantly with increasing platinum content. Thus, while electrode performance, as expressed by exchange current or current density, may be best in $\text{Pt}_{3.4}\text{W}$ [8], it may be advantageous to use somewhat lower platinum/tungsten ratios in order to attain longer lifetimes at higher temperatures.

Future work will study the grain growth rates of TiN electrodes and of Rh_2W electrodes.

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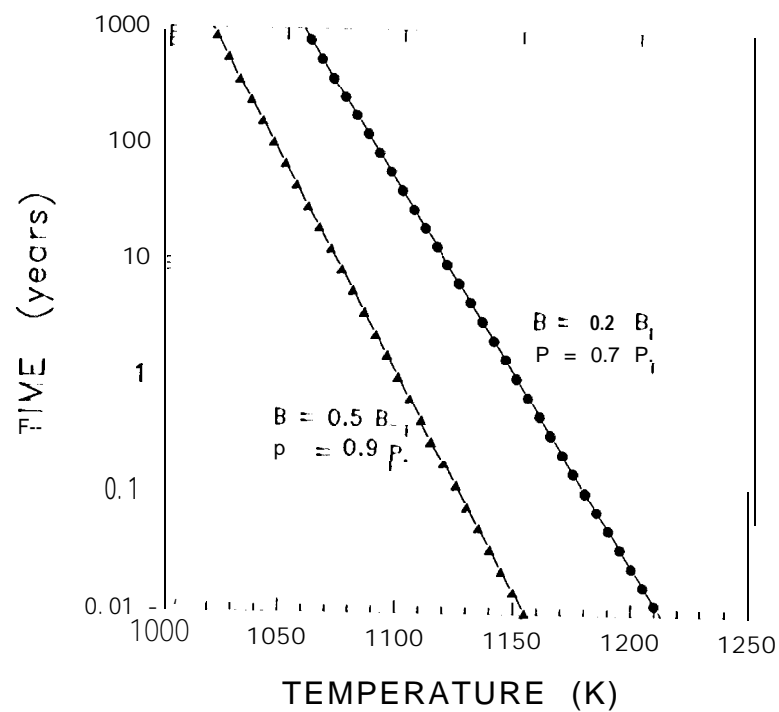


Figure 3: Predicted lifetimes for Mo electrodes if end-of-life grain diameter is $0.5 \mu\text{m}$ (A) or $1.0 \mu\text{m}$ (•).

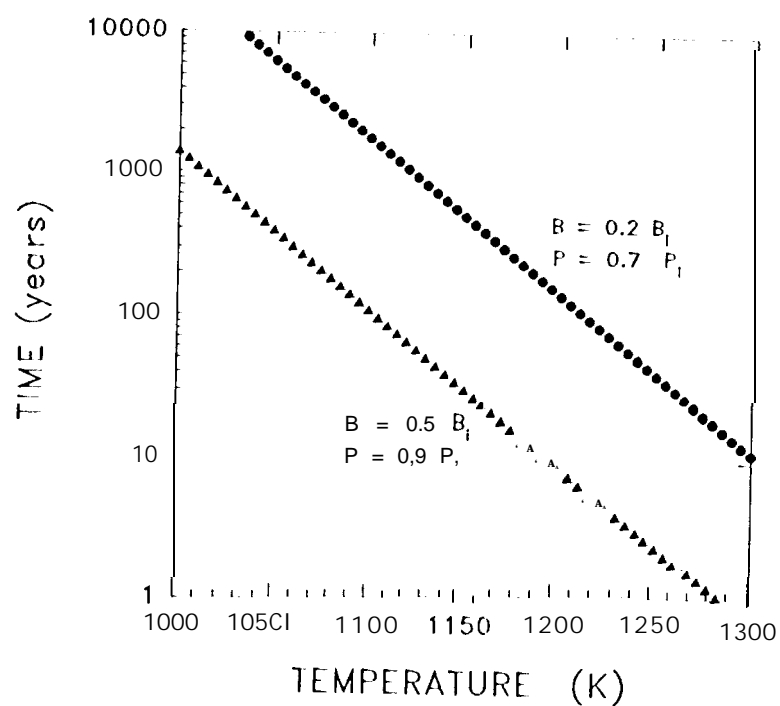


Figure 4: Predicted lifetimes for Pt_{23}W electrodes if end-of-life grain diameter is $0.5 \mu\text{m}$ (A) or $1.0 \mu\text{m}$ (•).